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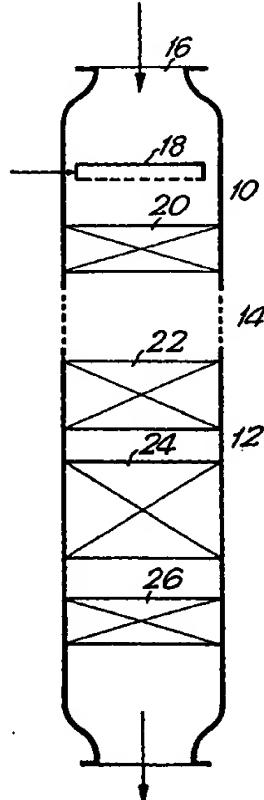
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(54) Title: IMPROVEMENTS IN PARTICULATE CONTROL

(57) Abstract

An improved system for treating the aftertreatment of exhaust gases, especially from diesel engines, comprises a first catalyst (20) effective to oxidise hydrocarbons, a second catalyst (22) effective to convert NO to NO<sub>2</sub>, a trap (24) for particulates, on which particulates may combust with the NO<sub>2</sub>, and optionally a NO<sub>x</sub> absorption material (26).



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## IMPROVEMENTS IN PARTICULATE CONTROL

5       The invention concerns improvements in emissions control, especially from internal combustion engines such as diesel and other lean-burn engines.

Lean-burn engines present problems in that it is difficult to reduce NO<sub>x</sub> emissions in the presence of oxygen. Compression ignition ("diesel") engines and some types of  
10 gasoline engines emit combustible particulate ('soot'). Although engine design, fuelling strategies and devices such as exhaust gas recirculation can decrease engine-out, NO<sub>x</sub> levels, it remains difficult to decrease both NO<sub>x</sub> and soot to below modern limits, such as are expected to be prescribed in European Stage IV regulations.

15       The difficulty appears to be greater for low exhaust gas temperatures, for example resulting from engine design such as light duty turbocharged direct injection diesel engines, especially if fitted with EGR, or from light duty generally.

However, there are a great many naturally aspirated diesel engines used throughout  
20 the world in vehicles, maritime craft and in stationary power sources. Although many modern engine designs utilise turbo-charging, there is a huge population of naturally aspirated engines, and this will be the case for the foreseeable future. Also, it is to be noted that in some countries, including particularly Japan, the performance enhancements from turbo-charging are not adjudged to be worthwhile, and indeed for  
25 some markets, turbo-chargers are removed from modern engines during truck or bus building or re-building. All diesel engines generate soot, but the soot from naturally aspirated engines is "wet" soot, that is it carries a considerable proportion of hydrocarbons absorbed into the particles. There are currently health concerns about the types of hydrocarbons absorbed on the soot. Although the present invention in another  
30 aspect has particular application to naturally aspirated diesel (compression ignition) engines, it may also find application in other engine designs which generate such particulates.

One particularly effective treatment for diesel exhaust is that marketed by  
35 Johnson Matthey PLC as the "Continuously Regenerating Trap" ("CRT" -RTM). In the

CRT system as disclosed in EP-A-0341832 an oxidation catalyst converts NO in the exhaust to NO<sub>2</sub>, the gas enriched with NO<sub>2</sub> is passed into a filter for the soot and the NO<sub>2</sub> causes facile combustion of the soot, thus continuously regenerating the filter and preventing blocking. The CRT is especially suited to so-called heavy-duty diesel engines as used in buses and larger trucks, where exhaust gas temperatures are generally relatively high.

In the case of turbo-charged direct injection engines used in light duty applications such as cars and light trucks, the exhaust gases are relatively cool, which with other factors makes the CRT system rather less effective than with heavy duty engines.

The invention provides a process of treating internal combustion engine exhaust gas containing O<sub>2</sub>, NO<sub>x</sub>, unburnt hydrocarbon ("HC"), CO and soot, comprising:

- 15 i. oxidising a substantial part of the HC, with possibly some oxidation of NO to NO<sub>2</sub>;
- ii. treating the product of step i to oxidise NO to NO<sub>2</sub>;
- iii. collecting soot; and
- iv. combusting the collected soot by reaction with the NO<sub>2</sub> and possibly any O<sub>2</sub> left over after steps i and ii.

The invention also provides a system for treating such internal combustion engine exhaust gas, comprising:

- 25 a first catalyst to receive engine exhaust gas and effective to promote oxidation of *inter alia* HC therein;
- a second catalyst receiving the product of the first catalyst and effective to promote oxidation of NO to NO<sub>2</sub>;
- a filter effective to collect soot and retain it until combusted by said NO<sub>2</sub> and possibly any O<sub>2</sub> left over after the first and second catalyst.

30

Since the gas contains soot, the first and second catalysts are suitably supported on a structure permitting passage of fine solid particles. The structure preferably provides through passages, for example in a honeycomb having at least 50, possibly more, the range 100-900 cells/inch<sup>2</sup> being generally preferred, more preferably 100 to 400 cells/in<sup>2</sup>.

The honeycomb may be composed structurally of ceramic or metal. Such ceramic may be for example alumina, silica, titania, zirconia or combinations such as example cordierite or silicon carbide. Such metal may be for example a refractory steel for example 5 Fecralloy. Such metal may make it practicable to provide more passages per square inch, eg up to 1200. Alternative monolithic supports are available, and it is intended to include static fluid mixers and the like, as required and subject to routine testing.

The support structure carries a coating ('washcoat') of high-surface support 10 material for catalytically active components. For the first catalyst the coating and these components are chosen so that it is effective to remove substantially all the HC. (It will normally also effect oxidation of CO to CO<sub>2</sub> and, to some extent, of NO to NO<sub>2</sub>). We believe, although we do not wish to be confined to such belief, that removing gaseous HC before oxidising NO to NO<sub>2</sub> removes species inhibiting such NO oxidation. 15 Although part of the NO may be converted to NO<sub>2</sub> over the first catalyst, unconverted NO is more effectively converted over the second catalyst. In the second embodiment of the present invention, HC absorbed on "wet" soot is combusted over the first catalyst.

An effect of the first catalyst can be to increase the temperature at the inlet of the 20 second catalyst to a level at which the velocity of NO to NO<sub>2</sub> conversion is sufficient to provide more NO<sub>2</sub>: the subsequent soot combustion reactions are also then faster. The resulting temperature should not of course be in a range at which NO<sub>2</sub> formation is equilibrium limited.

25 In the first embodiment of the invention, it is desirable to obtain an adequate reaction rate over the first catalyst for the reaction of gaseous HC; its inlet temperature is preferably maximised by disposing that catalyst as close as possible to the engine outlet. Thus it is typically mounted in the cylinder block region, for example on the exhaust gas manifold before or after a turbo-charger if used. To attain or increase such temperature 30 rise, additional fuel eg diesel fuel, may be dosed upstream of the first catalyst and oxidised thereon. Alternatively or additionally, the engine inlet fuel injection profile may be adjusted to increase the HC, or more conveniently the CO, content of the raw exhaust gas. Preferably such measures to increase gas temperature continue to provide a lean gas composition. Enrichment with HC and/or CO may be continuous or, preferably,

intermittent and initiated upon the detection of appropriate exhaust gas conditions. However attained, the temperature at the outlet of the first catalyst stage is preferably at least 200°, and eg up to 500°C.

5

Preferably the first catalyst has a very low light-off temperature for both the CO and HC oxidation reactions. This is an additional benefit during parts of the engine operating cycle in which exhaust gas temperatures are temporarily low, eg during idle.

10 In the second embodiment, the first catalyst contains a component capable of oxidising hydrocarbons of the type absorbed on wet soot. Suitable forms of ceria are particularly indicated, and such catalysts may comprise other components, as well as preferably one or more platinum group metal catalyst dispersed on an oxide support, which in turn is desirably carried on a monolithic catalyst support.

15

A particularly preferred first catalyst for the second embodiment comprises platinum dispersed on ceria, or on a metal oxide washcoat which incorporates ceria. The platinum loading may be up to 200g/cuft. Other catalytic or promoting elements may also be present. The ceria may be present as a washcoat over a platinum-catalysed  
20 alumina or over another catalyst.

Whereas the second catalyst may have the same composition as the first, it is suitably designed to be more effective for the NO to NO<sub>2</sub> reaction, and the temperature and/or space velocity, for example, may be different as between the two catalysts. Thus  
25 the conditions for the HC oxidation and NO oxidation may be independently optimised. The temperature in the second catalytic step is preferably in the range 150 to 350°C. (Since oxidation of NO is not strongly exothermic, there is little difference between inlet and outlet temperatures).

30

In the catalysts the active material comprises generally a platinum group metal ("PGM"), especially platinum and/or palladium, optionally with others eg rhodium. The exact composition of the catalyst is chosen to suit local requirements. Desirably they have relatively high (eg 10-150 g/ft<sup>3</sup>) loadings of platinum, and optionally may have other catalyst components such as rhodium or palladium or catalyst promoter

compounds.

The soot filter may be any capable of collecting the soot without causing excessive back-pressure. Its detailed specification is chosen according to the particular  
5 engine characteristics and the regulations to be met. It may be a ceramic wall flow filter, a ceramic foam filter, ceramic fibre filter, sintered metal or wire mesh filter of any suitable type. It may provide for removal of 50 to 100%, preferably at least 60%, more preferably 85%, or greater, of the measured soot in the exhaust gas. There may be a fail-safe bypass or a two-stage filter to cater for a situation where the filter would otherwise  
10 be blinded or blocked under certain engine operating conditions. If desired, the filter may be catalysed or part-catalysed to assist combustion. A variety of catalysts are known to be suitable, and these include one or more oxides of vanadium, cerium, and mixed Cs/La/V oxide and supported PGMs. The invention includes the possibility of initiating combustion of the soot if required, for example if the engine operating conditions are  
15 such that considerable soot is being/has been generated but the gas temperatures are rather too low for significant combustion; for example initiation may be by providing electric heating of a portion of the filter. The soot is generally carbon and/or heavy hydrocarbons, and is converted to carbon oxides and steam.

20 It is desirable to use low sulphur-content diesel fuel, suitably below 50ppms, and more preferably "ULSD" or ultra-low sulphur diesel of 10ppms or lower.

The invention provides also an engine in combination with a system as herein defined and a process of operating such an engine.

25 In this combination, in the first embodiment the first catalyst may be disposed close to the source of exhaust gas, to obtain a maximum convenient operating temperature and reaction rate therein. The outlet gas from that catalyst may undergo cooling, for example in a non-insulated or finned pipe, before entering the second catalyst.

30

In the combination of the second embodiment, the first catalyst is suitably disposed close to, desirably in, the same housing or "can", as the second catalyst and the filter. It is possible to contemplate a single catalyst monolith or "brick", one end of which carries the first catalyst, and the other end of which carries the second

catalyst, providing appropriate catalyst design and catalyst manufacturing technology is used, and providing that gas flow rates and space velocities are suitable.

5       The combination may include expedients such as EGR.

The combination may include sensors for at least one of: fuel composition; air/fuel ratio at engine inlet; exhaust gas compositions at critical stages; pressure drop. If engine inlet adjustment and/or fuel injection is used, then a temperature sensor after the  
10 first catalyst, and possibly before that catalyst and/or at the inlet of the NO oxidation catalyst are preferably provided. The control system may include also indicator means informing the engine operator, computer means effective to evaluate the data from the sensor(s), and control linkages effective to adjust the engine to desired operating conditions taking account of eg start-up, varying load and chance fluctuations, and to  
15 inject fuel into the exhaust gas if desired.

Preferably the engine is a diesel engine, although other engines, including direct injection gasoline engines, may also benefit from the invention. The engine may be the motive power for a vehicle, or may be a stationary power source or auxiliary power  
20 source. Most usefully the first embodiment is applied to a light duty engine as defined above, especially powering a passenger car or light truck or van. Generally "light" means less than 3500kg unladen weight. This may typically correspond to a cylinder capacity up to 6.0 litres and a power output up to 300 KW. The invention is potentially of value for engine for other duties. Desirably, the second embodiment is applied to "heavy duty  
25 diesel" engines.

It is believed, although we do not wish to be restricted by any theory, that the system and process of preferred embodiments of the invention, whilst permitting combustion of hydrocarbons in the first zone, generates sufficient NO<sub>2</sub> in the second  
30 zone to provide the right balance of NO<sub>2</sub> to carbon for combustion in the particular trap, under typical diesel operating conditions.

If desired, the present invention may be combined with additional means to reduce NO<sub>x</sub> in the gases leaving the system of the invention, which may include one or

both of NO<sub>x</sub> reduction catalysts, including catalysts of the three-way type or systems incorporating reductant addition and a suitable catalyst, and a regenerable absorber. Such means are generally known.

5

The first embodiment of the invention is illustrated with reference to the accompanying drawings, in which: figure 1 is a schematic drawing of a system according to the invention; figure 2 is a graph comparing the conversions of NO to NO<sub>2</sub> in the presence of HC (prior art) and absence of HC (invention).

10

Referring to figure 1, a light-duty turbocharged direct-injection diesel engine (not shown) discharges its exhaust, containing *inter alia* HC and soot, into a system comprising reactors 10 and 12, connected together for gas flow at region 14. Region 14 is shown by pecked lines to indicate that the connection may be short or may be relatively long, for example with reactor 10 at the engine outlet and reactor 12 under the vehicle body. Such a long connection may itself provide cooling or may include a finned region. Reactor 10 optionally includes at its inlet 16 the sparging spray injector 18. It essentially includes bed 20, of catalyst primarily for oxidation of HC and CO, the HC content of the gas entering bed 20 being HC exhausted by the engine, possibly augmented by HC injected at 18. Control means (not shown) responsive to the temperature of the gas leaving bed 20 regulates engine inlet conditions and HC injection at 18, to keep the temperature of bed 20 high enough for sufficiently rapid HC oxidation.

Reactor 12 contains at its inlet the bed 22 of catalyst primarily for oxidation of NO to NO<sub>2</sub>. The gas leaving bed 22, enriched in NO<sub>2</sub>, passes into soot filter 24, where soot is trapped and oxidised by reaction with the NO<sub>2</sub> and O<sub>2</sub>. Beds 22 and 24 constitute a "CRT" system. The gas, now substantially soot-free, may pass out to atmosphere if air quality regulations permit. Optionally the system may include, in the same reactor or possibly in a separate one, bed 26, charged with NO<sub>x</sub> absorption material, possibly with an injector (not shown) for reductant or ammonia between 24 and 26, and possibly with a catalyst for reduction of NO<sub>x</sub> to N<sub>2</sub>.

Each bed in the system is in the form of a ceramic honeycomb, with (except filter 24) an alumina washcoat carrying active material.

## EXAMPLE 1

A synthetic exhaust gas of the following composition v/v was used:

5

	CO <sub>2</sub>	4.5 %
	H <sub>2</sub> O	4.5 %
	O <sub>2</sub>	12.0 %
	CO	200 ppm
10	NO	400 ppm
	C <sub>3</sub> H <sub>6</sub>	0 or 400ppm or 800ppm
	N <sub>2</sub>	balance.

This was passed over a 1% w/w platinum on gamma alumina catalyst in particle form in  
15 a laboratory reactor at temperatures between 150°C and 500°C. This reactor is known to represent a typical exhaust catalyst consisting of platinum on an alumina washcoat on a honeycomb. The compositions of the outlet gas are shown in figure 2.

The plots for gas containing 400ppm and 800ppm HC (propylene) show there is  
20 very little conversion below about 200°C. However, in the absence of hydrocarbon (as removed in bed 20), already there is 20% conversion at 150°C and 85% conversion at 200°C. It is evident that once the HC (represented by C<sub>3</sub>H<sub>6</sub>) has been removed in the first oxidation step the oxidation of NO to NO<sub>2</sub> can take place more completely, affording more NO<sub>2</sub> for the combustion of particulate in the subsequent step of CRT.  
25 Bearing in mind the cool exhaust gas temperatures met with in modern light duty diesel engine designs, the significantly improved conversion at temperatures below 200°C resulting from the removal of gaseous HC, is particularly useful.

## EXAMPLE 2

30

The exhaust of a 4 cylinder turbocharged direct injection Diesel engine of 2.5 litre capacity with EGR and operated at an air-fuel weight ratio of about 30 was fed to the first of 2 catalytic stages of a system as shown in fig 1 of the drawings. The inlet exhaust gas composition v/v was:

	CO <sub>2</sub>	5.0%
	H <sub>2</sub> O	4.9%
	O <sub>2</sub>	13.0%
5	CO	800 ppm
	NO	100 ppm
	N <sub>2</sub>	balance

Catalysts 20 and 22 comprised platinum group metal supported on an alumina-containing washcoat on a 400 cpsi cordierite honeycomb. Catalyst 20 was mounted just outside the engine exhaust manifold after the turbo-charger; catalyst 22 was 1.0m downstream in an underfloor position. For some runs this was adjusted by injection of Diesel fuel using sparger 18, giving a lower but still lean air/fuel ratio. Comparative runs were carried out using at 20 another sample of the same washcoated honeycomb but without catalytic material. Runs were made at a range of load levels, giving temperatures in the range of 225° to 325°C, measured at 22 inlet. The outlet gas was analysed for NO, and total NOx and NO<sub>2</sub> calculated by difference. The table shows the concentration of NO and NO<sub>2</sub> at representative temperatures.

	Temp °C	225°		275°		325°	
		N oxide	NO	NO <sub>2</sub>	NO	NO <sub>2</sub>	NO
No Fuel	Cat	82	5	78	36	68	63
	Non-cat	96	1	80	18	70	54
+ Fuel	Cat	71	3	73	33	84	42
	Non-cat	65	3	78	26	88	36

20

It is evident that, except at the lowest temperature in presence of added fuel, the use of the first stage catalyst gives a significantly higher concentration of NO<sub>2</sub>, thus providing for more efficient combustion of collected soot on filter 22.

25

The second embodiment of the invention is now exemplified below. A variety of

typical oxide catalyst supports, in particulate form, were impregnated with Pt at the wt% shown in Table 1, using aqueous solution of Pt salts, by the incipient wetness technique.

The powdered samples were dried in air at 90°C. All samples were then calcined at  
5 500°C for 3 hours in air.

The samples were impregnated with standard commercial diesel engine lubricating oil at 10wt% per sample, and physically mixed to absorb the oil. Thermo-Gravimetric Analysis and Differential Thermal Analysis was performed on approx 40 mg  
10 samples using a STA 1500 machine using an air atmosphere, at a ramp rate of 10°C/min. The temperature of onset of combustion was determined, and the area under the DTA peak (expressed on a time basis, and normalised for sample weight) gives a relative measure of the oil combusted versus oil volatilisation. A TGA/DTA plot of a sample of the lubrication oil showed that volatilised occurred between ca 240 and 400°C, and that  
15 combustion occurred above ca. 400°C. The results for ceria and γ-alumina are shown below in Table 1.

Table 1

20	Exp	Sample	Pt-loading	DTA Onset	DTA
			(Wt%)	Temp (°C)	Peak Area (μV-S/mg sample)
	1	γ-alumina	0.0	226	1098
	2	γ-alumina	0.25	209	1108
25	3	ceria	0.0	134	2104
	4	ceria	0.009	138	2165
	5	ceria	0.0375	140	2125
	6	ceria	0.25	132	2361

30 It can be seen that both samples of γ-alumina have a relatively high DTA onset temperature, but all samples of ceria show a very significant reduction, into the range of temperatures commonly met with in diesel exhaust gases. All the ceria-based tests illustrate significant combustion of the hydrocarbon oil at low temperatures.

Additional tests were carried out in essentially the same manner, but using mixtures of ceria and platinum catalysed  $\gamma$ -alumina, with one or both of the ceria and alumina impregnated with 10 wt% of oil. The results are shown in Table 2 below:

5

Table 2

No.	Sample	Pt( $\text{Al}_2\text{O}_3$ ) Loading (wt%)	DTA Onset Temp ( $^{\circ}\text{C}$ )	DTA Peak Area
10				
1	Ceria <sup>OIL</sup> /alumina	0.25	147	1182
2	Ceria/alumina <sup>OIL</sup>	0.25	159	1147
3	Ceria <sup>OIL</sup> /alumina <sup>OIL</sup>	0.25	156	1355
4	(ceria/alumina) <sub>OIL</sub>	0.25	148	1915

15

The beneficial effect of the presence of ceria can be seen in all samples.

**CLAIMS**

1. A process of treating internal combustion engine exhaust gas containing O<sub>2</sub>, NO<sub>x</sub> unburnt hydrocarbon ("HC"), CO and soot, comprising:
  - 5 i. oxidising a substantial part of the HC, with possibly some oxidation of NO to NO<sub>2</sub>;
  - ii. treating the product of step i to oxidise NO to NO<sub>2</sub>;
  - iii. collecting soot; and
  - iv. combusting the collected soot by reaction with the NO<sub>2</sub> and possibly any O<sub>2</sub> left over after steps i and ii.
- 10 2. Process according to claim 1 in which at least steps i and ii are effected catalytically.
- 15 3. Process according to claim 1 or claim 2 carried out over:
  - i a first catalyst adapted to be fed with engine exhaust gas and effective to promote oxidation of HC therein;
  - ii a second catalyst adapted to be fed with the product of i and effective to promote oxidation of NO to NO<sub>2</sub>;
  - 20 iii a filter effective to collect soot and to retain it until combusted by said NO<sub>2</sub> and any O<sub>2</sub> left over after catalyst i and ii.
4. Process according to claim 3 in which the catalysts are honeycomb-supported.
- 25 5. Process according to claim 4 in which the cell density of the honeycomb is in the range 100-900 per square inch.
6. Process according to any one of the preceding claims, wherein the HC is in gaseous form.
- 30 7. Process according to claim 6 in which the first oxidation is carried out close to the source of exhaust gas, whereby to obtain a maximum convenient operating temperature and reaction rate.

8. Process according to claim 6 or claim 7 in which the gas leaving step/catalyst i undergoes cooling and then enters step/catalyst ii.
- 5 9. Process according to any one of the claims 6,7, and 8, including the provision of combustible upstream of the step catalyst i, whereby to increase the temperature at which that step operates.
10. 10. Process according to claim 9 in which said combustible is provided by modifying engine settings to pass more HC and/or generate more CO.
11. 11. Process according to any one of the claims 6 to 10 in which the first catalyst has a very low light-off temperature for HC and CO oxidation.
- 15 12. 12. A process according to any one of claims 1 to 5, wherein the HC is absorbed on the soot.
13. 13. Process according to any one of the preceding claims including also NOx-removal downstream of soot combustion.
- 20 14. 14. Process according to claim 13 including also a regenerable NOx absorber downstream of the collecting trap.
15. 25. 15. Process according to claim 14 including catalytic NOx-removal downstream of the NOx absorber.
16. 30. 16. System for carrying out a process according to any one of the preceding claims comprising:
  - i. a first catalyst to receive engine exhaust and effective to promote oxidation of HC therein;
  - ii. a second catalyst receiving the product of the first catalyst and effective to promote oxidation of NO to NO<sub>2</sub>;
  - iii. a filter effective to collect soot and to retain it until combusted by reaction with said NO<sub>2</sub> and, depending upon conditions, any O<sub>2</sub> left over after the first

catalyst.

17. System according to claim 16 in which the catalysts are honeycomb-supported.

5 18. System according to claim 17 in which the cell density of the honeycomb is in the range 100-900 per square inch.

19. A diesel engine in combination with a system according to any one of claims 16 to 18 connected to its exhaust.

10

20. An engine according to claim 19 which is one designed for light duty applications.

15 21. An engine according to claim 20 which is of the turbocharged direct injection type.

22. An engine combination according to claim 19, which is a heavy duty engine.

20

23. An engine combination according to claim 22, wherein the first catalyst is positioned close to the second catalyst.

24. An engine combination according to claim 23, wherein the first catalyst and the second catalyst are at opposite ends of a single catalyst monolith.

Fig.1.

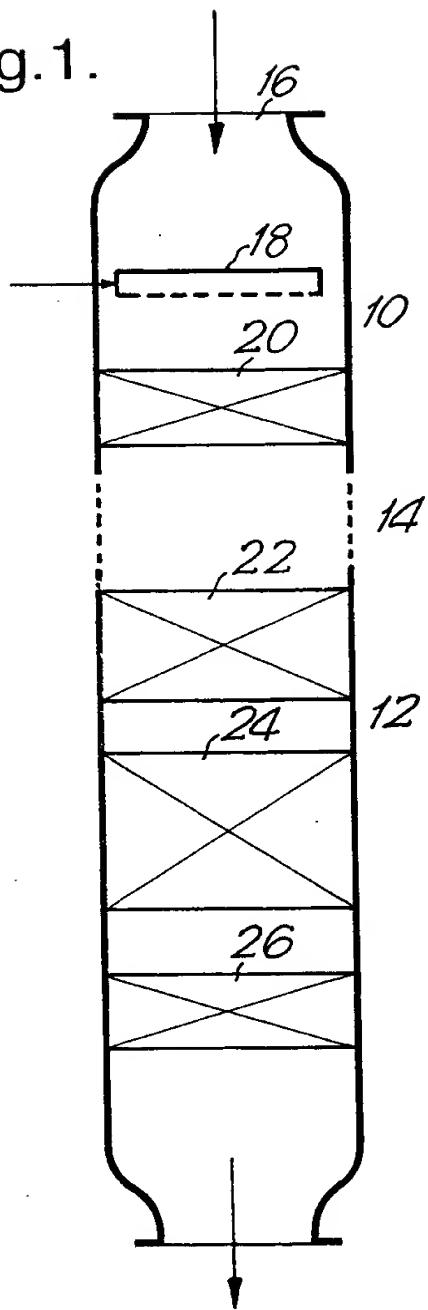
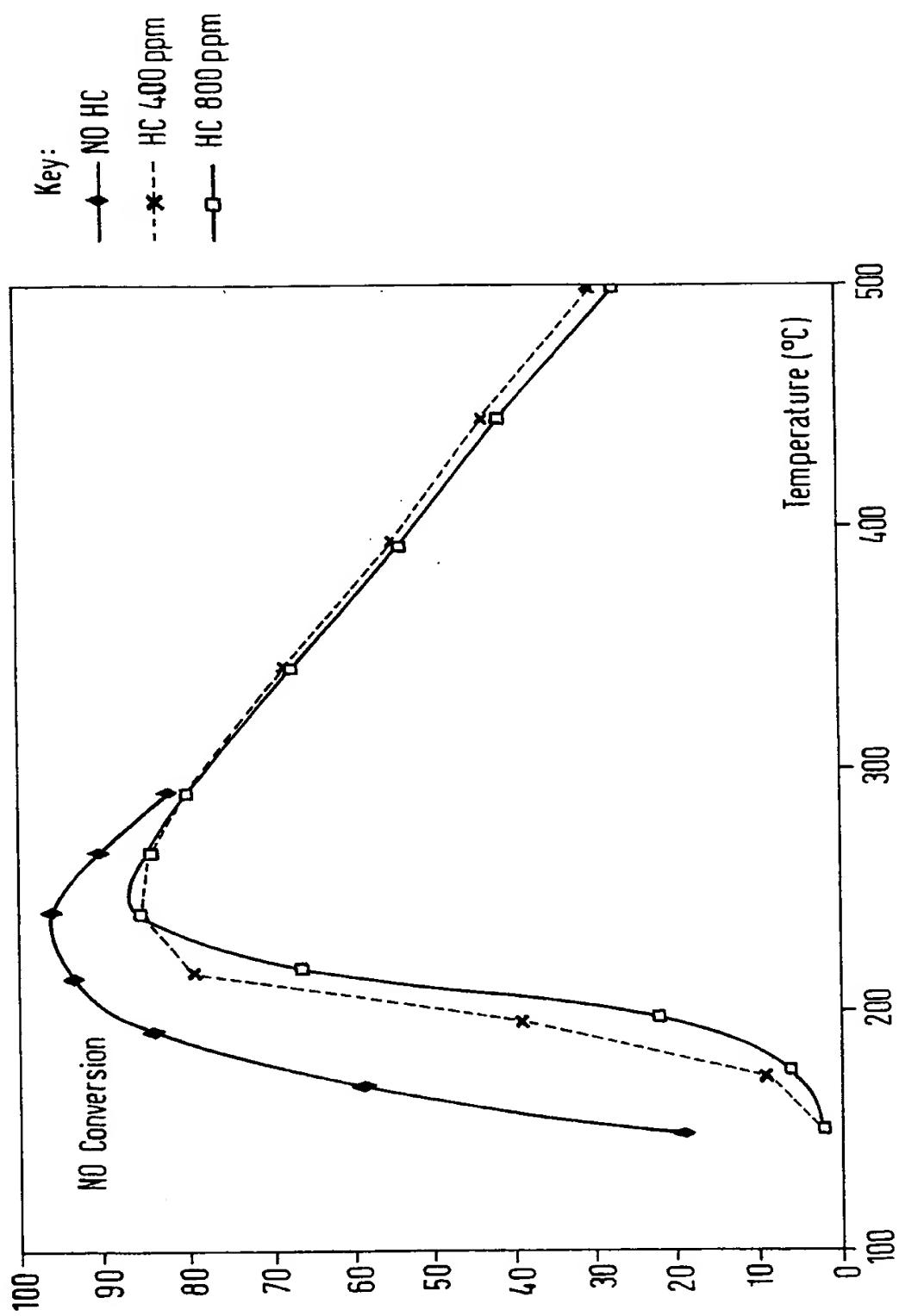


Fig.2.



## INTERNATIONAL SEARCH REPORT

D. International Application No

PCT/GB 99/03971

**A. CLASSIFICATION OF SUBJECT MATTER**  
 IPC 7 F01N3/28 F01N3/08 F01N3/02

According to International Patent Classification (IPC) or to both national classification and IPC

**B. FIELDS SEARCHED**

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 F01N

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the International search (name of data base and, where practical, search terms used)

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 5 743 087 A (ZAHN WOLFGANG ET AL) 28 April 1998 (1998-04-28)  column 2, line 8 -column 8, line 23; figures	1-4, 6-8, 11, 16, 17, 19, 20, 22, 23
A	EP 0 835 684 A (JOHNSON MATTHEY PLC) 15 April 1998 (1998-04-15) the whole document	1, 4, 16, 17, 19, 20
A	EP 0 341 832 A (JOHNSON MATTHEY INC) 15 November 1989 (1989-11-15) cited in the application page 2, line 42 -page 4, line 12; figures	1, 4, 16, 17, 22
A	EP 0 758 713 A (TOYOTA MOTOR CO LTD) 19 February 1997 (1997-02-19)	1-4, 14, 15
		-/-

Further documents are listed in the continuation of box C.

Patent family members are listed in annex.

## \* Special categories of cited documents :

- "A" document defining the general state of the art which is not considered to be of particular relevance
- "E" earlier document but published on or after the International filing date
- "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- "O" document referring to an oral disclosure, use, exhibition or other means
- "P" document published prior to the International filing date but later than the priority date claimed

- "T" later document published after the International filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- "Z" document member of the same patent family

Date of the actual completion of the International search

17 February 2000

Date of mailing of the International search report

24/02/2000

## Name and mailing address of the ISA

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Authorized officer

von Arx, H

## INTERNATIONAL SEARCH REPORT

Ref. No. / Serial Application No.  
PCT/GB 99/03971

## C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	GB 2 188 559 A (DRACHE KERAMIKFILTER) 7 October 1987 (1987-10-07)	
A	EP 0 749 774 A (NGK INSULATORS LTD) 27 December 1996 (1996-12-27)	
A	DE 33 37 903 A (REIF GERHARD;BAUM WERNER) 9 May 1985 (1985-05-09)	

## INTERNATIONAL SEARCH REPORT

Information on patent family members

Int'l Application No

PCT/GB 99/03971

Patent document cited in search report		Publication date		Patent family member(s)		Publication date
US 5743087	A	28-04-1998		DE 4406648 C US 5556604 A		10-08-1995 17-09-1996
EP 0835684	A	15-04-1998		JP 10159552 A NO 974706 A		16-06-1998 14-04-1998
EP 0341832	A	15-11-1989		US 4902487 A AT 132940 T DE 68925382 D DE 68925382 T DK 233389 A ES 2081301 T GR 3018800 T IE 71167 B JP 1318715 A NO 891936 A,B,		20-02-1990 15-01-1996 22-02-1996 15-05-1996 14-11-1989 01-03-1996 30-04-1996 29-01-1997 25-12-1989 14-11-1989
EP 0758713	A	19-02-1997		JP 9053442 A US 5746989 A		25-02-1997 05-05-1998
GB 2188559	A	07-10-1987		DE 3608635 A		17-09-1987
EP 0749774	A	27-12-1996		JP 9000872 A EP 0908225 A US 5884473 A		07-01-1997 14-04-1999 23-03-1999
DE 3337903	A	09-05-1985		NONE		

## PATENT COOPERATION TREATY

ADN  
Not phase ?  
etc ..

From the  
INTERNATIONAL PRELIMINARY EXAMINING AUTHORITY

To:  Wishart, Ian C. JOHNSON MATTHEY TECHNOLOGY CENTRE Blounts Court Sonning Common Reading RG4 9NH GRANDE BRETAGNE	<b>RECEIVED</b> 8 AUG 2000 NOTIFICATION OF TRANSMITTAL OF THE INTERNATIONAL PRELIMINARY EXAMINATION REPORT (PCT Rule 71.1)	PCT
		Date of mailing (day/month/year) 07.08.2000
Applicant's or agent's file reference AA 1403 PCT	<b>IMPORTANT NOTIFICATION</b>	
International application No. PCT/GB99/03971	International filing date (day/month/year) 29/11/1999	Priority date (day/month/year) 05/12/1998
Applicant JOHNSON MATTHEY PUBLIC LIMITED COMPANY et al.		
<p>1. The applicant is hereby notified that this International Preliminary Examining Authority transmits herewith the international preliminary examination report and its annexes, if any, established on the international application.</p> <p>2. A copy of the report and its annexes, if any, is being transmitted to the International Bureau for communication to all the elected Offices.</p> <p>3. Where required by any of the elected Offices, the International Bureau will prepare an English translation of the report (but not of any annexes) and will transmit such translation to those Offices.</p> <p>4. <b>REMINDER</b></p> <p>The applicant must enter the national phase before each elected Office by performing certain acts (filing translations and paying national fees) within 30 months from the priority date (or later in some Offices) (Article 39(1)) (see also the reminder sent by the International Bureau with Form PCT/IB/301).</p> <p>Where a translation of the international application must be furnished to an elected Office, that translation must contain a translation of any annexes to the international preliminary examination report. It is the applicant's responsibility to prepare and furnish such translation directly to each elected Office concerned.</p> <p>For further details on the applicable time limits and requirements of the elected Offices, see Volume II of the PCT Applicant's Guide.</p>		
Name and mailing address of the IPEA/   European Patent Office D-80298 Munich Tel. +49 89 2399 - 0 Tx: 523656 epmu d Fax: +49 89 2399 - 4465	Authorized officer  Murphy-Minehane, B Tel. +49 89 2399-2753	

PATENT COOPERATION T  
TY

## PCT

INTERNATIONAL PRELIMINARY EXAMINATION REPORT  
(PCT Article 36 and Rule 70)

Applicant's or agent's file reference <b>AA 1403 PCT</b>	<b>FOR FURTHER ACTION</b>	See Notification of Transmittal of International Preliminary Examination Report (Form PCT/IPEA/416)
International application No. <b>PCT/GB99/03971</b>	International filing date (day/month/year) <b>29/11/1999</b>	Priority date (day/month/year) <b>05/12/1998</b>
International Patent Classification (IPC) or national classification and IPC <b>F01N3/28</b>		
<p><b>Applicant</b>  <b>JOHNSON MATTHEY PUBLIC LIMITED COMPANY et al.</b></p>		
<p>1. This international preliminary examination report has been prepared by this International Preliminary Examining Authority and is transmitted to the applicant according to Article 36.</p> <p>2. This REPORT consists of a total of 5 sheets, including this cover sheet.</p> <p><input type="checkbox"/> This report is also accompanied by ANNEXES, i.e. sheets of the description, claims and/or drawings which have been amended and are the basis for this report and/or sheets containing rectifications made before this Authority (see Rule 70.16 and Section 607 of the Administrative Instructions under the PCT).</p> <p>These annexes consist of a total of sheets.</p>		
<p>3. This report contains indications relating to the following items:</p> <ul style="list-style-type: none"> <li>I <input checked="" type="checkbox"/> Basis of the report</li> <li>II <input type="checkbox"/> Priority</li> <li>III <input type="checkbox"/> Non-establishment of opinion with regard to novelty, inventive step and industrial applicability</li> <li>IV <input type="checkbox"/> Lack of unity of invention</li> <li>V <input checked="" type="checkbox"/> Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement</li> <li>VI <input type="checkbox"/> Certain documents cited</li> <li>VII <input type="checkbox"/> Certain defects in the international application</li> <li>VIII <input checked="" type="checkbox"/> Certain observations on the international application</li> </ul>		

Date of submission of the demand <b>23/06/2000</b>	Date of completion of this report <b>07.08.2000</b>
Name and mailing address of the international preliminary examining authority:  <b>European Patent Office D-80298 Munich Tel. +49 89 2399 - 0 Tx: 523656 epmu d Fax: +49 89 2399 - 4465</b>	Authorized officer <b>Zebst, M</b> Telephone No. +49 89 2399 7313



**INTERNATIONAL PRELIMINARY  
EXAMINATION REPORT**

International application No. PCT/GB99/03971

**I. Basis of the report**

1. This report has been drawn on the basis of (*substitute sheets which have been furnished to the receiving Office in response to an invitation under Article 14 are referred to in this report as "originally filed" and are not annexed to the report since they do not contain amendments.*):

**Description, pages:**

1-11                   as originally filed

**Claims, No.:**

1-24                   as originally filed

**Drawings, sheets:**

1/1                   as originally filed

2. The amendments have resulted in the cancellation of:

- the description,       pages:  
 the claims,              Nos.:  
 the drawings,           sheets:

3.  This report has been established as if (some of) the amendments had not been made, since they have been considered to go beyond the disclosure as filed (Rule 70.2(c)):

4. Additional observations, if necessary:

(4)

**INTERNATIONAL PRELIMINARY  
EXAMINATION REPORT**

International application No. PCT/GB99/03971

**V. Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement**

**1. Statement**

Novelty (N)                  Yes: Claims 1-24  
                                No: Claims

Inventive step (IS)           Yes: Claims 1-24  
                                No: Claims

Industrial applicability (IA) Yes: Claims 1-24  
                                No: Claims

**2. Citations and explanations**

**see separate sheet**

**VIII. Certain observations on the international application**

The following observations on the clarity of the claims, description, and drawings or on the question whether the claims are fully supported by the description, are made:

**see separate sheet**

**INTERNATIONAL PRELIMINARY  
EXAMINATION REPORT - SEPARATE SHEET**

International application No. PCT/GB99/03971

**Re Item V**

1. The industrial applicability of the invention seems to be self-evident (Article 33(4) PCT).
2. Reference is made to the following document:  
D1:EP-A-0341832 (cited in the application)
3. Claim 1

3.1. Novelty

The document D1 is regarded as being the closest prior art to the subject-matter of claim 1 and shows (the references in parentheses applying to this document):

*a process of treating internal combustion engine exhaust gas containing O<sub>2</sub>, NO<sub>x</sub>, unburnt hydrocarbon ("HC"), CO and soot, with the following steps:*

- a) *oxidising NO to NO<sub>2</sub>;*
- b) *collecting soot; and*
- c) *combusting the collected soot by reaction with the NO<sub>2</sub> and possibly any O<sub>2</sub> left over after step a* (page 2, lines 43-55).

The subject-matter of claim 1 therefore differs from this known process in that, before step a) is set a previous step in which "*a substantial part of the HC is oxidised, with possibly some oxidation of NO to NO<sub>2</sub>*", which product is treated to oxidise NO to NO<sub>2</sub> in the next step a) in reference to document D1.

The subject-matter of claim 1 is therefore novel (Article 33(2) PCT).

3.2. Inventive step

The problem to be solved by the present invention may therefore be regarded as to adapt the "CRT system" disclosed in D1, suited to so called heavy-duty engines, in light duty engines where in contrary, the exhaust gases are relatively cool. The inclusion of this previous step in the process of document D1 is not known nor obvious from any document of the search report, nor comes within the scope of the customary practice of the skilled person. Consequently, the process of claim 1 involves an inventive step (Article 33(3)) PCT).

(6)

**INTERNATIONAL PRELIMINARY  
EXAMINATION REPORT - SEPARATE SHEET**

International application No. PCT/GB99/03971

**4. Dependent claims 2 to 15**

This claims are dependent on claim 1 and as such also meet the requirements of the PCT with respect to novelty and inventive step.

**5. Claims 16 to 18**

Since the subject matter of claim 16 relates to a **system** including all the technical features of the invention, which are "specifically designed" for carrying out a process according to any of the claims 1 to 15 and since the contribution over the prior art (the subject matter of claim 16 differs from the known system of document D1 in that, a "*first catalyst*" is inserted in the exhaust path between the engine and "*catalyst (1) - second catalyst*" in order to "*receive engine exhaust and effective to promote oxidation of HC therein*") corresponds to the contribution the process (in accordance with claims 1 to 15) makes over the prior art, claim 16 also fulfils the requirements of articles 33(2)(3) PCT.

The claims 17 and 18 are dependent on claim 16 and as such also meet the requirements of the PCT with respect to novelty and inventive step.

**6. Claims 19 to 24**

Since claim 19 relates to a **diesel engine in combination with a system** to any one of the claims 16 to 18, the subject-matter of this claim is also new and involves an inventive step (Articles 33(2)(3) PCT).

The claims 20 to 24 are dependent on claim 19 and as such also meet the requirements of the PCT with respect to novelty and inventive step.

**Re Item VIII**

The dependent claims 20 and 21 refer to **an engine** which is not in accordance with claim 19, who is directed to a **diesel engine in combination with a system** and therefore create obscurity of the subject-matter to be protected (Rule 6.4 PCT).